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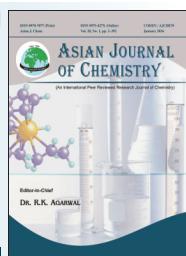
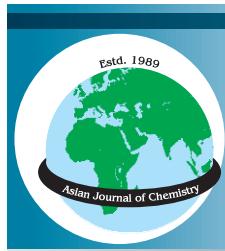
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1 Removal of High Concentration of Methyl *tert*-Butyl ether in Synthetic 2 Wastewater by Employing High Frequency Ultrasound Waves

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8 In this study, the proposed ultrasound technique at high frequency 2.4 MHz for methyl *tert*-butyl ether (MTBE) removal has investigated.
9 The ultrasonic removal mechanism of methyl *tert*-butyl ether in aqueous solution is complex because of the competition between hydroxyl
10 radical attack, pyrolysis and hydrolysis reactions. A detailed investigation of MTBE removal using sonolysis has performed here with a
11 kinetics models study. Chemical destruction by sonolysis is rationalized using hydroxyl radical chemistry, in which MTBE transfers into
12 the cavitating bubbles and decomposed. The kinetics study indicates that the removal of MTBE at different initial concentration namely
13 (2000, 1000 and 500 ppm) is the best fitted with first order kinetic model with a reaction rate constant of 0.034 min⁻¹. The removal of
14 MTBE investigated at different reactant volumes inside the ultrasound reactor found that the lower volume of reactant is preferable on
15 higher volume. The results of MTBE removal show that more than 85 % has obtained, at only 50 min of exposing to ultrasound irradiation
16 even with high initial concentrations.

17 **Keywords:** Ultrasound, Degradation, Methyl *tert*-butyl ether, Wastewater treatment.

INTRODUCTION

18 Methyl *t*-butyl ether (MTBE) has been used as a fuel
19 oxygenate worldwide due to its good properties as octane
20 enhancers and helping in preventing engine knocking. Methyl
21 *tert*-butyl ether was firstly used in the USA since 1979 to
22 replace tetra-ethyl lead which was known to its serious effect
23 on human health resulted from air borne pollution. Since that
24 date and over decades of years MTBE has been used as an
25 octane enhancer and fuel oxygenation additive in gasoline to
26 provide a cleaner burning fuel. Despite the several technological
27 benefits of using MTBE [1-5], but recently there is
28 warning sign of having a serious environmental problem with
29 regard to water quality [6-10]. Methyl *t*-butyl ether has become
30 one of the most common contaminants in shallow ground
31 waters and drinking water, mainly as a consequence of petroleum
32 leakage from underground tanks [11]. Methyl *t*-butyl ether
33 according to USEPA classification is considered a risk chemical
34 compound on human health with a high potential of carcinogen
35 [11]. The environmental fate of MTBE depends closely on its
36 excellent solubility in water and its very low soil sorption
37 coefficient [9,12,13]. This means that MTBE is only retained
38 by soil layers in a weak concentration and is rapidly transported

39 to ground waters. Another reason for MTBE's persistence to
40 be more mobile in groundwater systems than other gasoline
41 components If groundwater is moving gradually downward,
42 the chemicals dissolved in it will also gradually move
43 downward, because MTBE may migrate over greater distances,
44 the magnitude of dive may be greater [6,11].

45 Several studies have reviewed the different technologies
46 used to the treatment or removal of MTBE from underground
47 water. These technologies may include both *ex situ* technologies
48 (pump and treat) and *in situ* technologies (airsparging,
49 bioremediation, chemical oxidation, phytoremediation and
50 monitored natural attenuation) [14-17]. Methyl *tert*-butyl ether
51 can be biologically degraded under both aerobic and anaerobic
52 conditions and both *in situ* and *ex-situ*, however, removal of
53 MTBE can be incomplete, resulting in the formation of *tert*-
54 butyl alcohol (TBA). Generally, aerobic conditions have been
55 shown to be far more effective in the complete biological
56 treatment and removal of these compounds but still expensive
57 [18-21].

58 The use of ultrasound technology to remove or decomposi-
59 tion of MTBE is still under investigation [22]. Matouq *et al.*
60 [1-5] have employed the use of high frequency of ultrasound
61 wave for the removing of different pollutants from wastewater,

62 the use of such process to decompose of MTBE under high
 63 frequency is a new technique. Kim *et al.* [23] for example have
 64 studied the removal of MTBE and other oxygenated fuel, by
 65 employing the ultrasound at low frequency in the presence of
 66 saturated oxygen with detailed removal mechanisms proposed
 67 for each gasoline oxygenate. They reported that the common
 68 degradation pathways involve abstraction of α -hydrogen atoms
 69 by hydroxyl radicals generated during ultrasound cavitation at
 70 low temperature. The ultrasound at either low or high frequency
 71 will be a new area for researchers to investigate since the process
 72 of MTBE removal by conventional remediation technologies,
 73 is costly and ineffective. Therefore, much attention will be focused
 74 on other methods such as advanced oxidation processes (AOPs)
 75 [24,25] and ultrasound techniques for its degradation; to
 76 explore its usefulness.

77 Still there are very few studies deal with the degradation
 78 of MTBE at high frequency of ultrasound more than 1 MHz
 79 [23] that directly applied to a solution of MTBE and water. In
 80 this study, the process of using such ultrasound techniques
 81 will be introduced here to investigate the ability of ultrasound
 82 wave to remove MTBE at high concentration. The use of ultra-
 83 sound with high frequency alone in the removal of MTBE
 84 from is a new topic, here both the removal and the kinetics
 85 of MTBE removal will be investigated using a simulated
 86 wastewater.

EXPERIMENTAL

87 Methyl *tert*-butyl ether obtained with 99 % purity from
 88 Saudi Basic Industries Corporation, (SABIC) (www.sabic.com)
 89 Table-1 summarizes these properties. The experimental results
 90 analysis performed using gas shromatography PYE-UNICOM
 91 4900-FID, with a stainless steel column 2 m long and 2 mm
 92 diameter, filled with chromosrob C03 as packing material. The
 93 detection temperature was set at 300 °C and the injection set
 94 250 °C while the oven was set at 200 °C. Calibration of a gas
 95 chromatography device was done carefully with a solution
 96 with a known amount of MTBE. The results are then plotted
 97 generating a calibration curve as a reference for future results.
 98 After that, different concentration samples of MTBE were
 99 prepared.

TABLE-1
MTBE PROPERTIES BY SABIC

Parameter	Unit	Quantity
Purity	wt %	98 min
C4-hydrocarbons	wt %	0.5 max
C5-hydrocarbons	wt %	1 max
Methanol	wt %	0.7 max
<i>tert</i> -Butyl alcohol	wt %	0.6 max
Di-isobutene	wt %	0.6 max
Water	ppm	500 max

Sources: <http://www.sabic.com/corporate/en/productsandservices/chemicals/mtbe>

100 In 1 L, volumetric flask a measured amount of pure MTBE
 101 is added to in order to obtain the target concentration needed.
 102 The required concentrations in this study was adjusted at 2000,
 103 1000 and 500 ppm by volume (v/v %). These concentrations
 104 are corresponding to 1480.8, 740.4 and 370.2 ppm by mass

105 respectively. The usual concentration of MTBE in water is
 106 actually less than of those specified above concentrations, in
 107 order to investigate the ability of ultrasound to remove MTBE
 108 at high concentration with very short period. Ray *et al.* [26] 109
 investigated the reduction of MTBE in groundwater with an
 110 initial concentration of 1300 (µg/L) ppm to decompose into
 111 final concentration of 20 ppm or less, this value is which one
 112 specified by USEPA [27].

113 A 50 mL sample with certain concentration of MTBE 114 placed in a cylindrical tube reactor attached with ultrasound
 115 cell at the bottom. The solution irradiated with ultrasound 116 for a fixed period around 50 min. Each 10 min a sample with a
 117 syringe (0.5 mL), was taken from the solution and directly
 118 injected to the gas chromatography for analysis. To prevent
 119 any MTBE escape from the solution to the atmosphere a watch
 120 glass fitted at the top of the cylindrical reactor as shown in
 121 Fig. 1.

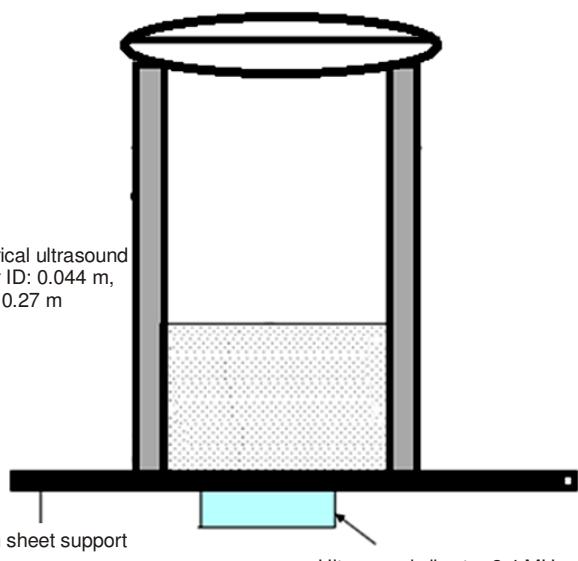


Fig. 1. Experimental setup for cylindrical ultrasound reactor

122 The experimental apparatus demonstrated in Fig. 1, which 123 consists of a cylindrical vessel with 44 mm inside diameter and 124 270 mm height. Watch glass cover attached to the cylindrical. 125 Electrical source with variable voltage supply rages from 0 to 126 40 volts was attached to the apparatus. The electrical supply 127 can also be adjusted to control the electrical current source 128 from 0 to 600 mA. All experiments conducted at 24 volts and 129 500 mA, according to the specified condition by ultrasound 130 device wave generator manufacture. Ultrasonic vibrator 131 comprised of 20 mm diameter transducer, which contains 132 piezoceramics (sandwich) with titanium end masses leading 133 the face from which the ultrasonic emitted. It has a frequency 134 of 2.4 MHz and electric input power 9.5 Watt and it supplied 135 by Honda electronics Co. Ltd., of Japan, type HM-2412.

RESULTS AND DISCUSSION

136 Fig. 2 shows the concentration profile for MTBE removal 137 at 2.4 MHz ultrasound waves and 50 mL volume of MTBE as 138 solution. This figure shows that the profiles are decreasing 139 with the increasing of time for three different concentrations,

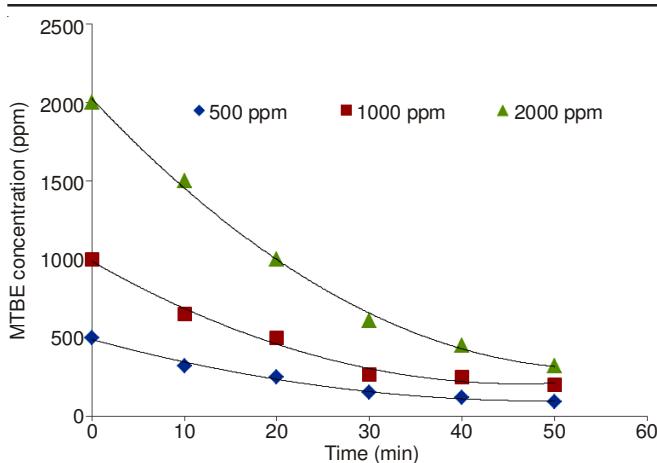


Fig. 2. Concentration profiles for MTBE removal at 2.4 MHz ultrasound waves and 50mL volume of MTBE

140 2000, 1500, 500 ppm. This means that MTBE in the solution
 141 is removing with time due to the effect of irradiation by
 142 ultrasound. The final solution tested by gas chromatography
 143 didn't show any sign of other compounds which means MTBE
 144 should have either been broken down into gaseous molecules
 145 or degraded into water or both. Literature suggests that it is
 146 possible for MTBE to be oxidized into CO_2 and water [28].
 147 The results of MTBE removal shown in Fig. 2, indicates that
 148 the when the MTBE concentration at higher the removal is
 149 almost the same for MTBE at lower concentration. For example
 150 when the initial concentration of MTBE is 2000 ppm and after
 151 50 min the concentration reaches 318 ppm with more than 84
 152 % removal. However, when the initial concentration of MTBE
 153 of 500 ppm the final concentration reaches 90 ppm and after
 154 50 min with a removal parentage of 81 %. This percentage of
 155 removal in such short time is acceptable to reach the standard
 156 regulation for MTBE in groundwater according to USEPA,
 157 bearing in mind that in actual case the initial concentration of
 158 MTBE does not reach the investigated concentration in this
 159 study.

160 The effect of changing the liquid volumes inside the
 161 ultrasound reactor on removal of MTBE is shown in Fig. 3 at
 162 three different volumes 50, 40 and 30 mL. It is clear from the
 163 figure that the relation between the removal rate and the liquid
 164 volume inside the ultrasound reactor is an inverse function.
 165 When the liquid volume (solution level) was 50 mL (for the
 166 different MTBE concentrations 2000, 1000 and 500 ppm) the
 167 removal of MTBE reaches more than 80 % for all MTBE
 168 concentration at 50 mL volume, compared to more than 95 %
 169 for all MTBE concentrations, at 30 mL liquid volume and
 170 after 50 min. Therefore, the removal process of MTBE under
 171 ultrasound effect is more preferable toward a low volume inside
 172 the ultrasound reactor.

173 **Chemical kinetic removal models:** The suitable chemical
 174 removal model will be investigated here in which the process
 175 will be tested for different kinetics order. The obtained results
 176 fitted with different kinetics models namely first and second
 177 order. The following simulation will show the best results
 178 fitting for the obtained experimental results.

179 **First order kinetics model:** In this model the experi-
 180 mental data were fitted according to simple first order rate:

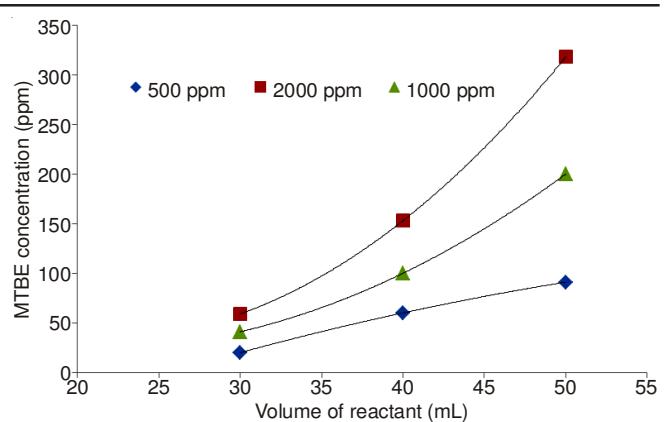


Fig. 3. Effect of changing MTBE volume inside Reactor after 50 min of irradiation at different initial concentration

$$C(t) = C_0 e^{-k_1 t} \quad (1) \quad 181$$

To obtain a liner fitting eqn. 1 rearranged to: 182

$$\ln C(t) = \ln C_0 - k_1 t \quad (2) \quad 183$$

where k (min^{-1}) is the first order rate constant can be estimated from the slope by plotting $\ln C(t)$ versus time (t) as shown in Fig. 4. The figure shows a consistency between the plotted experimental data and the proposed model kinetics, where the correlation factor (R^2) is higher than 98 %. 184
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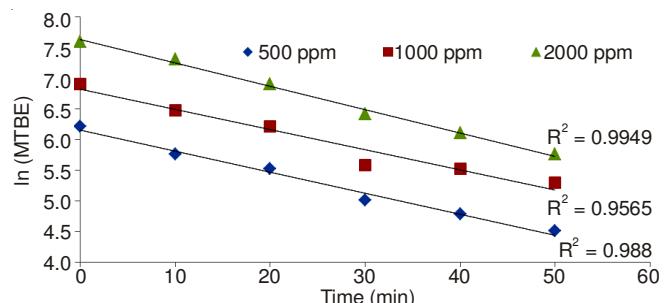


Fig. 4. First order model results fitting at 50 mL liquid volume and constant frequency wavelength of 2.4 MHz at different concentrations of MTBE

Second order kinetics model: The proposal of having a second order kinetic model will be examined here. The change in the removal concentration can be fitted by using the second order kinetic equation model described by eqn. 3: 189
190
191
192

$$-r = \frac{dC}{dt} = -kC^2 \quad (3) \quad 193$$

For liner fitting the equation can be rearranged as: 194

$$\frac{1}{C} = kt + \frac{1}{C_0} \quad (4) \quad 195$$

where k is the second order removal rate constant and it can be estimated from the slope after plotting $1/C$ vs. t . as demonstrated in Fig. 5. 196
197
198

The experimental result shows that the fitted $1/C$ versus t , for different initial concentrations of MTBE. Although the fitting looks in a good consistency, still the R^2 , for the first order is higher for all experimental data at different initial concentrations. This means in this experimental work and at these conditions the best kinetics model for the removal of 199
200
201
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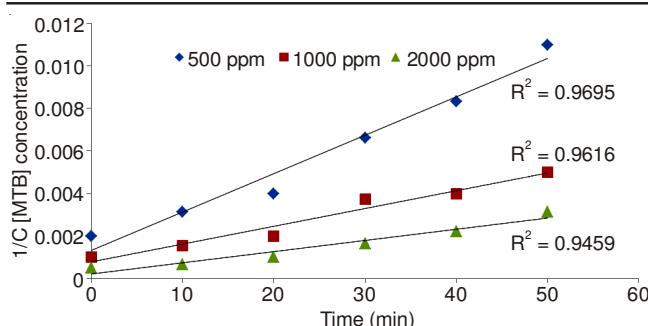


Fig. 5. Second order model data fitting at 50 mL liquid volume and constant frequency wave length of 2.4 MHz at different concentrations of MTBE

205 MTBE at 2.41 MHz ultrasound is best fitted with a first order
206 kinetics. The average reaction rate constant is estimated to be
207 0.035 min^{-1} according to results obtained from Fig. 4, at first
208 order. Table-2 summaries the reaction rate constant at different
209 initial concentrations of MTBE.

TABLE-2
REMOVAL RATE CONSTANT AT DIFFERENT INITIAL
CONCENTRATION OF MTBE AND 50 mL VOLUME
SOLUTION AND 2.4 MHZ ULTRASOUND

Initial concentration of MTBE (ppm)	$k (\text{min}^{-1})$
2000	0.038
1000	0.033
500	0.034

210 Conclusion

211 The removal of methyl *tert*-butyl ether by employing the
212 high frequency of ultrasound has successfully obtained. The
213 experimental conditions selected in this study is fixed at three
214 different MTBE initial concentrations (2000, 1000 and 500
215 ppm), with three different volume solutions at ultrasound
216 reactor volume (50, 40 and 30 mL) has given a good results
217 for removal of MTBE within in a short period, during the
218 irradiation process. The results show that MTBE removal
219 process at 2.4 MHz and after only 50 min has exceeded 85 %
220 of its initial concentration. The results also demonstrate that
221 the removal could be obtained at lower initial liquid volume
222 30 mL, regarding to the initial concentration of MTBE, since
223 the percentage of removal is almost the same for three different
224 initial concentrations. The kinetics model study shows that
225 removal of MTBE is following the first order kinetics model
226 with reaction rate constant k equal to $0.035 (\text{min}^{-1})$.

REFERENCES

1. M.A.-D. Matouq and Z.A. Al-Anber, *J. Ultrasonics Sonochem.*, **14**, 393 (2007).
2. M. Matouq, Z.A. Al-Anber, T. Tagawa, S. Aljbour and M. Al-Shannag, *Ultrason. Sonochem.*, **15**, 869 (2008).

3. M. Matouq, N. Susumu, Z. Al-Anber, O. Markarian, O. Al-Ayed, T. Tagawa, *Res. J. Pharmaceut. Biol. Chem. Sci.*, **5**, 940 (2014).
4. M. Matouq, T. Tagawa and N. Susumu, *J. Global Network Environ. Sci. Technol.*, **16**, 805 (2014).
5. M. Matouq, Z. Al-Anber, N. Susumu, T. Tagawa and H. Karapanagioti, *Separ. Purif. Tech.*, **135**, 42 (2014).
6. P.B.L. Chang and T.M. Young *Water Res.*, **34**, 2233 (2000).
7. M.D. Einarson and D.M. Mackay, *Environ. Sci. Technol.*, **35**, 66A (2001).
8. EFOA (The European Fuel Oxygenates Association), 2001, <http://www.efoa.org>.
9. J.W. Antony, Methodology to evaluate natural attenuation of MTBE, in: B.C. Alleman, A. Leeson (Eds.), *Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds*, Columbus Batelle Press, 1999, pp. 121–133.
10. J. Jacobs, J. Guertin and C. Herron, *MTBE: Effects on Soil a Groundwater Resource*, Lewis Publishers, Boca Raton, 2001.
11. P.J. Squillace, J.F. Pankow, N.E. Korte and J.S. Zogorski, *Environ. Toxicol. Chem.*, **16**, 1836 (1997).
12. B.C. Alleman and A. Leeson, eds., *Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds*, Columbus Batelle Press, 1999, pp. 121–133.
13. A. Azadpour-Keeley, 2002. *Envirogen Propane Biostimulation Technology for In-Situ Treatment of MTBE-Contaminated Ground Water*," EPA/600/R-02/092. On the Internet at <http://www.epa.gov/ORD/NRMRL/Pubs/600R02092/600R02092.pdf>.
14. C.L. Bruce, C.D. Gilbert, R.L. Johnson and P.C. Johnson, 1998. "Methyl *tert*-Butyl Ether Removal by In Situ Air Sparging in Physical Model Studies," in *Proceedings, First International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, Calif., May 18–21, pp. 293–98. Columbus, Ohio: Battelle Press.
15. A.P. Mortensen, K.H. Jensen, T.O. Sonnenborg and E. Arvin, *Ground Water Monit. Remediat.*, **20**, 87 (2000).
16. K.W. Rutherford and P.C. Johnson, *Ground Water Monit. Remediat.*, **16**, 132 (1996).
17. P.C. Johnson, *Environ. Sci. Technol.*, **32**, 276 (1998).
18. T.C. Schmidt, M. Schirmer, H. Weiß and S.B. Haderlein, *J. Contam. Hydrol.*, **70**, 173 (2004).
19. R.J. Steffan, K. McClay, S. Vainberg, C.W. Condee and D. Zhang, *Appl. Environ. Microbiol.*, **63**, 4216 (1997).
20. M.I. Stefan, J.R. Mack and J.R. Bolton, *Environ. Sci. Technol.*, **34**, 650 (2000).
21. X.R. Xu, Z.Y. Zhao, X.Y. Li and J.D. Gu, *Chemosphere*, **55**, 73 (2004).
22. D.K. Kim, K.E. O'Shea and W.J. Cooper, *Sci. Total Environ.*, **430**, 246 (2012).
23. D.K. Kim, K.E. O'Shea and W.J. Cooper, *Ultrason. Sonochem.*, **19**, 959 (2012).
24. A.A. Burbano, D.D. Dionysiou, M.T. Suidan and T.L. Richardson, *Water Res.*, **39**, 107 (2005).
25. W.M. Glaze, J.W. Kang and D.H. Chapin, *Ozone Sci. Eng.*, **9**, 335 (1987).
26. A.B. Ray, A. Selvakumar and N.T. Anthony, 2003, "Treatment of Methyl *Tertiary*-butyl Ether (MTBE) Contaminated Waters with Fenton's Reagent", Urban watershed Management Branch, United State Environmental Protection Agency.
27. USEPA, 1997, "Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl *Tertiary*-butyl Ether (MTBE)", EPA 822-F-97-008, Office of Research and Development, Washington D. C.
28. C. Guillard, N. Charton and P. Pichat, *Chemosphere*, **53**, 469 (2003).